Development of an Ion-Implanted Phosphorus in Silicon SRM for the Semiconductor Industry

Silicon is the foundation material of the electronic age, lying at the base of the 200 billion dollar world-wide semiconductor industry. Silicon's properties are manipulated by precise implantation and distribution of other atoms (dopants), which makes the accurate measurement of impurity distributions imperative. SEMATECH (a consortium of semiconductor manufacturers) recently listed Standard Reference Material (SRM) implant of phosphorus in silicon as a high priority industrial need.

The U.S. semiconductor industry relies heavily on secondary ion mass spectrometry (SIMS) for characterization of the depth distribution of dopants in silicon. To achieve high accuracy in the concentration determination by SIMS, standards of known dopant concentration, conveniently provided by ion implants of certified dose, are required. Standard Reference Materials of boron and arsenic implants in silicon (SRMs 2137 and 2134 [1]) have already been developed by NIST as SIMS calibration standards.

The SIMS community in the United States undertook a round-robin study to calibrate the implanted dose of phosphorus in silicon by consensus. Dose determinations among laboratories varied by nearly a factor of 2, reflecting primarily the errors of the respective in-house standards (Fig. 1). These results demonstrate the need for a common phosphorus reference material to improve inter-laboratory reproducibility.

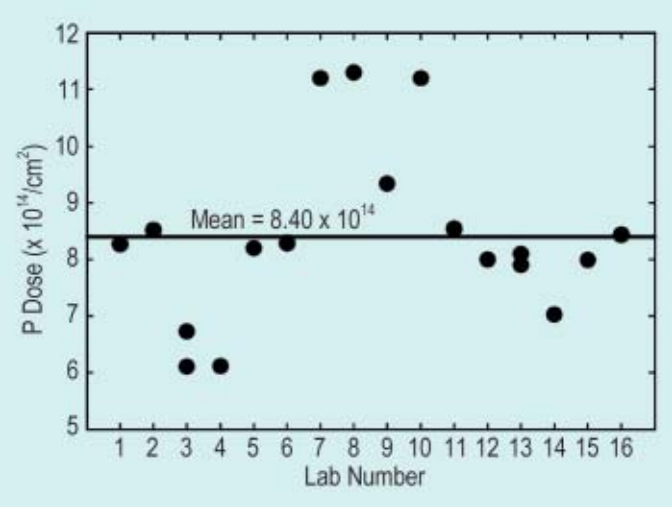

Fig. 1. Round-robin measurements of phosphorus in silicon by secondary ion mass spectrometry in 16 U.S. industrial laboratories, demonstrating the need for a common phosphorus reference material to improve inter-laboratory reproducibility.

In pursuit of a phosphorus in silicon SRM, a radiochemical neutron activation analysis (RNAA) procedure has been developed, critically evaluated, and shown to have the necessary sensitivity, chemical specificity, matrix independence, and precision to certify phosphorus at ion implantation levels in silicon [2, 3]. During sample irradiation, ^{31}P undergoes neutron capture to form ^{32}P, which is then separated from the matrix and measured by beta counting. The procedure is used here to assign a value to the quantity of phosphorus in SRM 2133 (phosphorus implanted silicon).

SRM 2133 was prepared by phosphorus implantation of a 200 cm diameter silicon wafer. The wafer was cut into 1 cm^2 pieces by means of a wafer saw, and twelve pieces were chosen for analysis. The area of each piece was determined by measuring its dimensions using a digital micrometer. During irradiation, ^{32}P may be produced via neutron capture by the implanted phosphorus, by bulk phosphorus impurity in the wafer, and by silicon. The latter two sources lead to measurement error, which must be corrected. These corrections were made by measuring silicon blanks, which were prepared by cutting a non-implanted silicon wafer into ~ 1 cm^2 pieces. Standards were prepared by deposition of standardized solutions of phosphorus on aluminum foils.

Samples, standards, and blanks were irradiated for 3 hours in irradiation tube RT1 of the NIST neutron source at a neutron fluence rate of 1.05 x 10^{14} $cm^{-2}{\cdot}s^{-1}$. Targets were then processed using the method developed previously [2, 3]. Silicon samples and blanks were mixed with a few milligrams of non-radioactive phosphorus (carrier) and dissolved in a mixture of nitric and hydrofluoric acids. Phosphorus was separated from the matrix first by precipitation as ammonium phosphomolybdate, then as magnesium ammonium phosphate. The latter was collected by filtration, washed with dilute ammonium hydroxide and ethanol, air dried, weighed, and packaged for beta-ray counting. The yield, (fraction of recovered phosphorus carrier), was determined gravimetrically, assuming a composition of $MgNH_4PO_4{\cdot}6H_2O$. Standards were processed using a similar procedure.

Counting of ^{32}P ($t_{1/2}$ = 14.28 d) was performed using a beta proportional counter. Purity of the ^{32}P from other radionuclides was ascertained by gamma-ray spectroscopy, and by monitoring beta count rates over a period of four half lives. No discernible contamination from other radionuclides was noted. ^{32}P count rates were adjusted for decay time, blank correction, and for differences in beta self-absorption.

NIST currently certifies elemental concentrations in SRMs using one of three modes: (1) a primary method at NIST with confirmation by other method(s); (2) two independent critically evaluated methods at NIST, and (3) one method at NIST and different methods by outside collaborating laboratories. Certification using a primary method is only possible when all potentially significant sources of uncertainty have been evaluated explicitly for the application of the method and the matrix under investigation. Therefore, in order to certify the phosphorus concentration in SRM 2133 using RNAA as a primary method it was necessary to evaluate all significant sources of uncertainty explicitly. For this set of measurements, we considered sources of relative uncertainty greater than 0.01 % to be significant. The results of a complete evaluation of all sources of uncertainty are listed in Table 1. This evaluation yielded an expanded relative uncertainty of 1.27 % (as defined by ISO and NIST), and gives an approximate level of confidence of 95 %. The measured phosphorus concentration is $(9.55 \pm 0.12) \times 10^{14}$ atoms·cm^{-2}.

In conclusion, we have successfully applied RNAA as a primary method for the certification of this new SRM. The observed relative expanded uncertainty of 1.27 % is smaller than the 3 % value needed by the semiconductor industry. This new SRM should greatly enhance the U.S. semiconductor industry's ability to achieve accurate and reproducible analytical results for this key dopant in silicon.

Table 1. Individual Uncertainty Components for Determination of Phosphorus in SRM 2133.

Source of Uncertainty	Uncertainty (1σ) %
Measurement Replication ($\sigma/\sqrt{n}$)	0.31
Measurement Replication (Standards) ($\sigma/\sqrt{n}$)	0.47
Measurement of Sample Area	0.012
Blank Correction	0.022
Blank Correction (Standards)	0.019
Volumetric Calibrations (Standards)	0.12
Concentration of Standard Solution	0.15
Mass Standard Solution on Foil	0.037
Radiochemical Impurity	0.13
Beta Self-Absorption	0.07
Beta Self-Absorption (Standards)	0.08
Carrier Yield Determination	0.10
Self-Shielding	0.024
Irradiation Geometry	0.09
Combined Uncertainty	0.63
Coverage Factor	2.0
Expanded Uncertainty	1.27

References

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